

Platinum Catalyzed C-H Activation and the Effect of Metal-Support Interactions

Aaron Sattler,*[®] Michele Paccagnini,[®] Michael P. Lanci,[®] Sabato Miseo, and Chris E. Kliewer

Corporate Strategic Research, ExxonMobil Research & Engineering Company, 1545 Route 22 East, Annandale, New Jersey 08801, United States

Supporting Information

ABSTRACT: Catalytic C-H bond activation of methane and ethane on a series of silica supported platinum catalysts (Pt/SiO₂) was studied by using hydrogen/deuterium (H/D) exchange. Kinetic experiments demonstrate that under the reaction conditions studied, the rate of C-H bond activation shows approximate first order dependence in alkane and inverse first order dependence in D₂. The rate of C-H activation is affected by the presence of sodium on the silica support, where sodium-free supports have the fastest rates of C-H activation, as assessed by H/D exchange. CO adsorption and FTIR studies indicate that the Pt particles on the sodium-free support are more electron-deficient, having the most blue-shifted linear CO stretch, while sodium-containing supports are more electron-



donating, having the most red-shifted linear CO stretch. It is proposed, based on the results described in this article and previous work in the literature, that more electron-donating supports cause the Pt particles to be more electron-rich and to adsorb D^* (or H^*) more strongly, thereby stabilizing the ground state and resting state of the catalyst, resulting in a decreased rate of C-H activation.

KEYWORDS: H/D exchange, C-H activation, alkanes, mechanism, isotopes, deuterium

INTRODUCTION

Developing new technologies for converting alkanes selectively to higher value products is a major challenge for industrial catalysis, due to the relative kinetic and thermodynamic stability of alkanes and their C-H bonds.¹ Current routes typically implement high temperatures, exemplified by steam methane reforming to produce syngas (CO and H_2) or ethane steam cracking to produce ethylene. Oxidative routes remove thermodynamic limitations and high temperature requirements, but overoxidation (e.g., to CO_2) becomes a major problem.² New catalytic routes for alkane upgrading are, therefore, desired and understanding the mechanism(s) by which C-H activation occurs, a necessary step in any alkane transformation, can assist in catalyst development and discovery.^{3,4} Platinum (Pt) is a well-known and important metal for hydrocarbon catalysis,⁵ specifically alkane conversions, as exemplified by its industrial use in catalytic reforming to produce high-octane gasoline,⁶ propane dehydrogenation to produce propylene,⁷ and hexane aromatization to produce benzene.⁸ In this work, we sought to study the C-H bond activation step itself, a step that precedes the catalytic reactions mentioned above, and the effect of metalsupport interactions, by utilizing isotope exchange reactions with hydrogen and deuterium (H/D). Specifically, on a series of silica supported Pt catalysts, Pt/SiO₂, we have (i) identified a mechanism consistent with the observed kinetic data for C-H activation in both methane and ethane, and (ii) demonstrated that the presence of sodium (Na) on a silicasupport, which acts to modify the properties of the support thereby influencing metal-support interactions, affects the material's ability to activate C-H bonds. These results have connections with other catalytic reactions that have been studied in the past, where metal-support interactions have been implicated, and demonstrate the high sensitivity that H/D exchange in alkanes can have as a characterization tool for heterogeneous catalysts.

RESULTS AND DISCUSSION

A series of three silica-supported Pt catalysts (Pt/SiO_2) having sodium contents of either 0 or ~500 ppm of Na were synthesized (see Supporting Information, SI, for more details). All samples were loaded with ~0.75 wt % Pt by incipient wetness impregnation, using aqueous solutions of Pt tetraammine nitrate and arginine⁹ at a 1:8 molar ratio, dried and then calcined in air at 425 °C for 2 h. Calcination in air completely oxidized the arginine, which was verified by temperature-programmed oxidation and reduction experiments. The samples were then reduced in the reactor in H₂

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Tab	le	1. Sampl	e Descriptio	ns and	Characterization	of Pt	Particle	Size by	v Chemisorp	tion"
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	pt conc. (wt%)	alkali conc. (ppm)	dispersion O_2 (%) ^b	dispersion H_2 (%) ^c
Pt-0	0.75	<16	38(5)	35(5)
Pt-500	0.75	479	42(5)	46(5)
Pt-500S	0.75	500 (from IWI)	43(5)	38(5)

"Numbers in parentheses indicate two-standard deviations, i.e., 95% confidence intervals. ${}^{b}O_{2}$ chemisorption at 35 °C, assuming O:Pt_s = 1. ${}^{c}H_{2}$ chemisorption at 35 °C, assuming H:Pt_s = 1.

at 450 °C for 4 h. The 0 ppm of Na sample (Pt-0) used an ultrapure silica supplied by PQ Corporation where the sodium level was below the detection limit of the experimental techniques (<16 ppm). Two samples with ~500 ppm of Na sample were synthesized, which corresponds to an approximate 2:1 Pt:Na molar ratio; the first used Davisil 646 (Pt-500), where the 500 ppm of Na is introduced from impurities in the commercial silica. The second ~500 ppm sample (Pt-500S) was synthesized by treating the ultrapure silica with 500 ppm of NaNO₃, followed by calcination in air at 425 °C for 2 h, thereby removing the nitrate groups. While Pt-500 and Pt-500S both have the same loading of Na, the Na in Pt-**500S** is expected to be on the surface of the SiO_2 due to the synthetic procedure (S indicates surface in 500S). The samples were characterized by H_2 and O_2 chemisorption (Table 1)¹⁰ and transmission electron microscopy (TEM), which indicate similar Pt particle sizes (between 2.5 and 3.5 nm) in all the samples (see SI).

The ability of the Pt/SiO₂ materials to activate C–H bonds in methane and ethane was studied by using H/D exchange.^{11–13} Methane experiments are detailed below, and ethane experiments can be found in the SI. Using this technique, d₀-methane (CH₄) and D₂ contact a heterogeneous catalyst in a well-mixed batch reactor and undergo isotope exchange. The extent of reaction was monitored by using GC– MS (gas chromatography–mass spectrometry). H/D exchange of alkanes (e.g., conversion of CH₄ to CH₃D, Figure 1)

 $CH_4 \xrightarrow{D_2} CH_3D + CH_2D_2 + CHD_3 + CD_4$ $C_2H_6 \xrightarrow{D_2} C_2H_5D + C_2H_4D_2 + C_2H_3D_3 + C_2H_2D_4 + C_2HD_5 + C_2D_6$

Figure 1. $\rm H/D$ exchange in methane (top) and ethane (bottom) to produce deuterated isotopologues.

requires C-H bond activation and, therefore, the measured exchange rates reflect a catalyst's ability to cleave C-H bonds.

Exchange rates were measured at conversions of 50% or less and with excess D_2 (generally here: 100 Torr CH_4 and 800 Torr D_2) to limit the influence of unproductive C–H activation events (with HD or H_2) that do not result in the formation of new C–D bonds and the reverse reaction of CH_3D to form CH_4 . At higher conversions, mixtures of D_2 , H_2 , and HD exist (in addition to the different isotopologues of the alkanes); this does not change the intrinsic rate of C–H activation (ignoring isotope effects) but assessment by H/D exchange becomes more challenging as the molecules approach isotopic equilibration, and at equilibration no reaction can be observed.

The H/D exchange reaction progressions are shown in Figure 2 for CH₄/D₂, on Pt-500S, Pt-500, and Pt-0 catalysts, at the same catalyst loading (50 mg), temperature (275 °C), and initial partial pressures of CH₄ and D₂ (100 and 800 Torr, respectively). The three materials catalyze H/D exchange at different rates, as seen by the change in CH₄ concentration (i.e., partial pressure, P_{CH4}) over time, in the relative order Pt-0 > Pt-500 > Pt-500S (Figure 2). Similar data are shown in the SI for methane/D₂ exchange at other temperatures, in addition to ethane experiments, demonstrating that catalysts that contain sodium undergo H/D exchange more slowly compared with catalysts that are sodium free, under the experimental conditions studied.¹⁴

The rate of disappearance of CH_4 follows the first order equation (eq 1), allowing us to obtain k_{obs} for each experiment, which are normalized on a per mole of surface Pt atom basis.¹⁵ Experiments to assess reaction orders in CH_4 and D_2 , by changing their partial pressures and keeping the total system pressure constant, demonstrate that H/D exchange is approximately first order in CH_4 pressure and inverse first order in D_2 pressure, under the experimental conditions studied (Figure 3).^{16–18} Thorough studies on H/D exchange in ethane have been previously reported by Zaera and coworkers who made similar observations, finding a first order dependence on ethane and -0.55 order in D_2 .^{19–22} The focus



Figure 2. Monitoring H/D exchange between methane and D₂ on Pt/SiO₂ catalysts at 275 °C: CH₄ (black \bigcirc), CH₃D (red \square), CH₂D₂ (blue \diamondsuit), CHD₃ (green \triangle), and CD₄ (magenta \bigtriangledown).



Figure 3. Partial pressure dependence studies to determine k_{rxn} . CH₄: 100 Torr, D₂: 800 Torr (red \bigcirc); CH₄: 50 Torr, D₂: 800 Torr (blue \square); and CH₄: 100 Torr, D₂: 400 Torr (black \diamondsuit).

of the work here is to understand the effect of the support on C–H activation; although these data allow for analysis of rates of secondary C–H activations (i.e., multiple exchange), as has been shown previously,^{11,19} this is not within the scope of the present work.

These data allow for the determination of turnover frequencies (TOFs), in units of mols of CH₄ activated (i.e., mols of CH₄ molecules to undergo H/D exchange) per mol of surface Pt atom per second, which follow rate eq 2 based on the pressure dependencies above, where $k_{\rm rxn}$ is related to $k_{\rm obs}$ by eq 3. Thus, H/D exchange is informing us on the catalytic rate of C–H bond cleavage on this series of Pt catalysts, and the $k_{\rm rxn}$ values obtained are listed in Tables 2 and 3 for the

Table 2. Rate Constants (k_{rxn}, s^{-1}) Measured As a Function of Temperature for Pt/SiO₂ Catalysts

	methane			ethane		
temp. (° C)	Pt-500S	Pt-500	Pt-0	Pt-500S	Pt-500	Pt-0
150						0.6
175					0.5	1.3
200			0.2	0.2	1.3	7.1
225		0.4	1.3	0.7	5.8	24
250	0.2	1.9	4.7	2.2		
275	1.1	8.1	18	9.6		
300	3.9					

temperature dependence and partial pressure dependence studies, respectively.²³ These results clearly demonstrate that the support can affect the rate of C–H bond activation. Previous work has studied the exchange rate as a function of particle size and the differences in TOF observed here based on support are significantly larger than the minor differences previously observed due to particle size;^{11c-e} in fact, H/D exchange was shown to be structure insensitive when Pt dispersions are above 10%.^{11d} These prior findings help to support the notion that the different rates of C–H activation reported here are largely a function of the support tuning the metal active site electron-density, and not attributable only to minor differences in particle size as assessed by chemisorption and TEM. 24

A mechanism consistent with the observed rate law involves reversible dissociation of D_2 (k_1 and k_{-1} , K_D) on the catalyst surface to open up a set of sites (* = site), followed by C–H bond cleavage via dissociative adsorption $(k_2, the reverse of$ which is k_{-2}) to give R* (R = CH₃ or C₂H₅) and H* (Figure 4). H*/D* scrambling is rapid on the catalyst surface, and with an excess of D*, which is the situation at low conversions, C–D bond formation occurs via associative desorption (k_3) to form product, which is a deuterated alkane. This mechanism can be described by a bimolecular Langmuir-Hinshelwood process, as has been used in similar studies previously,^{19,18} and is shown in eq 4. Equation 4 can be transformed into eq 5 under conditions where (i) D₂ adsorption is significantly stronger than RH adsorption, (ii) we assume quasi-equilibrated and steady-state concentrations of adsorbed D* and CH3*, and (iii) that k_3 and k_{-2} are the same when isotope effects are ignored (i.e., both steps are $C^{-x}H$ bond formations, where x =1 or 2). Equation 5 reduces to eq 6 under these conditions and is consistent with our observed rate law (eq 2). Thus, the rate constant of H/D exchange (k_{rxn}) is a function of the equilibrium deuterium chemisorption (K_D) and the rate constant of C-H bond cleavage (k_2) on the Pt surface (eq 7), which informs us of the rate of C-H bond activation, not the rate of C–D bond formation, as k_3 , the rate constant of C-D bond formation is not in the rate law under the experimental conditions studied.

This effect holds true as long as the most abundant surface intermediate (MASI) is D*. Further evidence to support this is provided by (i) the inverse dependence of D₂, which indicates a D* covered surface that is energetically most favorable, (ii) if the R* was energetically more favorable than H*, then the surface would be primarily R* covered, which would be expected to give a rate law that has a zero order dependence in alkane,²⁵ which is not observed, and (iii) calorimetry experiments done by Campbell and co-workers that are in

Table 3. Rate Constants (k_{rxn}, s^{-1}) Measured as a Function of Alkane and D₂ Partial Pressure for Pt/SiO₂ Catalysts

	condition		methane			ethane		
alkane (Torr)	D_2 (Torr)	He (Torr)	Pt-500S (275 °C)	Pt-500 (250 °C)	Pt-0 (225 °C)	Pt-500S (225 °C)	Pt-500 (200 °C)	Pt-0 (175 °C)
100	800	0	1.1	2.9	1.2	0.54	1.3	1.3
100	400	400	0.9	2.8	1.1	0.44	1.3	1.3
50	800	50	1.1	2.7	1.3	0.58	1.4	1.3



Figure 4. Proposed mechanism of C–H activation and H/D exchange on Pt/SiO_2 catalysts (note: H* and D* are shown to represent the reaction mechanism, and do not indicate the actual number of H^*/D^* species).



Figure 5. Monitoring H/D exchange between methane and D₂ on Pt-500 at 225 °C, 250 °C, and 275 °C: CH₄ (black \bigcirc), CH₃D (red \square), CH₂D₂ (blue \diamondsuit), CHD₃ (green Δ), and CD₄ (magenta \bigtriangledown).

accord with a H* covered surface being more stable than a CH_3^* surface.²⁶ On the basis of their thermochemical measurements, an H* covered surface is approximately 14 kcal mol⁻¹ more enthalpically stable than a CH_3/H covered surface.²⁷

$$-\frac{d(P_{\rm CH_4})}{dt} = k_{\rm obs} P_{\rm CH_4} \tag{1}$$

$$\text{TOF} = \frac{k_{\text{ren}} P_{\text{CH}_4}}{P_{D_2}}, \text{ where TOF} = \frac{\text{mols of CH}_4 \text{ activated}}{\text{mols surface Pt atoms } \times \text{ sec}}$$
(2)

$$k_{\rm rxn} = k_{\rm obs} \left(\frac{V}{RT}\right) P_{\rm D_2} \tag{3}$$

$$TOF = k_3[CH_3^*][D^*]$$
 (4)

$$TOF = \frac{k_2 P_{CH_4}}{\left(1 + \frac{K_{CH_4} P_{CH_4}}{(K_D P_{D_2})^{1/2}} + (K_D P_{D_2})^{1/2}\right)^2}, \text{ where}$$

$$K_D = \frac{k_1}{k_{-1}}, K_{CH_4} = \frac{k_2}{k_{-2}}, \text{ and } k_3 = k_{-2}$$
(5)

TOF =
$$\frac{k_2 P_{\text{CH}_4}}{K_{\text{D}} P_{\text{D}_2}}$$
, when $K_{\text{D}} P_{\text{D}_2} \gg K_{\text{CH}_4} P_{\text{CH}_4}$ and 1 (6)

$$k_{\rm rxn} = \frac{k_2}{K_{\rm D}} \tag{7}$$

The H/D exchange rate dependence on temperature was studied (Figure 5). As expected, exchange rates increase with temperature, and Arrhenius analyses (Figure 6) allow for the determination of the apparent activation energies (E_{app}) and frequency factors (ln A), which are tabulated in Table 4. Pt-0 has the lowest E_{app} for methane (28 kcal mol⁻¹), while **Pt-500S** has the highest E_{app} (35 kcal mol⁻¹). The E_{app} for methane is higher than that of ethane,²⁸ which correlates with the C–H bond dissociation energies of the free alkanes (methane: 105.0 kcal mol⁻¹, ethane: 100.5 kcal mol⁻¹).²⁹ These results are consistent with large bodies of literature on H/D exchange of alkanes on metal catalysts, which show that H/D exchange of ethane is faster than methane.¹³ This is also consistent with the energy diagram in Figure 4, where the decreased rate in methane exchange compared to ethane is due to the difference in k_2 , while K_D is not affected. It is interesting to compare the $E_{\rm app}$ here with previous work from Iglesia and co-workers on (i) C–H activation of methane on bare Pt surfaces, where they



Figure 6. Arrhenius analysis for methane/ D_2 H/D exchange on Pt/SiO₂ catalysts.

measured ΔH^{\ddagger} of ~19 kcal mol^{-1,30,31} and (ii) hydrogen chemisorption isotherms, which indicate that H* adsorption is ~10 kcal mol^{-1,32} Thus, the sum of these two values is ~29 kcal mol⁻¹, which are the two steps implicated in this work for C–H activation, which is similar to the E_{app} observed here.^{33,34}

The above catalytic data suggest that metal-support interactions influence the material's ability to activate C-H bonds. To gain additional characterization on the Pt particles in the Pt/SiO₂ samples, the samples were analyzed by FTIR spectroscopy combined with CO adsorption (see SI for details). $^{35-39}$ The difference spectra (before and after treatment with 5% CO) are shown in Figure 7, and clear differences can be observed.⁴⁰ First, the linear CO stretching band shifts progressively to lower energy in the sodiumcontaining samples, from 2073 cm^{-1} for **Pt-0** to 2061 cm^{-1} for Pt-500S. In general, bands at lower energies (red-shifted) often indicate that the Pt particles are more electron-rich, as the increased electron density on Pt can backbond into CO antibonding orbitals, thereby decreasing the effective CO bond order and stretching frequency. As described above, the samples containing sodium are calcined prior to treatment with the Pt precursor, such that a sodium oxide like species forms. Sodium oxide species are more basic compared to silica, and the more basic material is more electron donating, thereby making the Pt particles more electron-rich and red-shifting the CO band. Previous work consistent with our results showed that potassium (K) on silica supported Pt materials caused red-shifts in the CO band. 41,42 Additional evidence for an electronic effect is provided by analysis of the linear and bridged CO species; as the support becomes more basic, the ratio of linear to bridged CO has been shown to decrease,⁴³ which is observed for the Pt/SiO₂ series here, as seen by the increase in the bridging CO band at $\sim 1800 \text{ cm}^{-1}$ for Pt-500S and Pt-500 (Figure 7).

In addition to silica systems, significant work has been done on basic-zeolite systems with different alkali exchanged zeolites, which has shown that exchange with alkali cations



Figure 7. FTIR difference spectra of CO adsorbed on Pt/SiO_2 materials (Pt-500S, red; Pt-500, black; Pt-0, blue).

(e.g., K, Cs) cause red-shifts in the CO adsorption band,^{44–57} and this area has been reviewed by Barthomeuf.⁵⁸ Dipole– dipole interactions have also been reported to cause shifts in the CO stretching frequency, and may be responsible for the different CO stretching frequencies observed.⁵⁹ In this regard, the CO stretching frequency as a function of coverage⁶⁰ was measured (Figure 8), and extrapolation to zero-coverage allows for estimation of the singleton frequency (Figure 9), the CO stretching frequency in the absence of CO–CO dipole–dipole coupling interactions. As can be seen in Figure 8, all linear CO stretching bands red-shift at lower coverage, such that **Pt-500S** is still red-shifted compared to **Pt-0** by about 23 cm⁻¹, in fact even more so than at high coverage (Δ cm⁻¹ = 12). These data support the hypothesis that sodium on the support results in electronic modification of the Pt particles.

This work has led us to one main question, which is why is C-H activation slower on Pt materials that contain sodium? Analysis of the energy diagram in Figure 4 helps us to address this question. Specifically, the rate of C-H activation is dependent on both (i) the ground state energy of the D* covered surface, which we can equate to an H* covered surface when ignoring isotope effects, and (ii) the transition state energy of an open set of sites interacting with a C-H bond to cleave and form R^{*} and H^{*} ($K_{\rm H}$ and k_2 , where $K_{\rm H} = K_{\rm D}$). Therefore, the samples containing sodium either (i) have lower ground state D^* (H*) surfaces, indicating stronger Pt-D(H) interactions with less modulation of the transition state energy, or (ii) have higher transition state energies where ground state modulation is less. Previous measurements by Dumesic and coworkers showed that hydrogen (and carbon monoxide) heats of adsorption were ~ 5 kcal mol⁻¹ greater for Pt particles on basic supports compared with acidic supports,⁶¹ which is in accord with scenario (i) where the ground state D* (H*) surface in Pt-500S is more stable than that of Pt-0. Campbell has also reported calorimetry data on metal-support

Table 4. Arrhenius Analysis of H/D Exchange Reactions on Pt/SiO₂ Catalysts^a

		methane		ethane			
	temp. range (° C)	$E_{\rm app}$ (kcal mol ⁻¹)	ln (A)	temp. range (° C)	$E_{\rm app}$ (kcal mol ⁻¹)	ln (A)	
Pt-500S	250-300	35 (1)	32 (1)	225-275	28 (1)	28 (1)	
Pt-500	225-275	32 (1)	31 (1)	175-225	22 (1)	24 (1)	
Pt-0	225-275	28 (1)	29 (1)	150-225	21 (1)	24 (1)	

^aNumbers in parentheses indicate two-standard deviations, i.e. 95% confidence intervals.



Figure 8. FTIR difference spectra of CO adsorbed on Pt/SiO₂ materials at varying CO coverages.



Figure 9. Extrapolation of linear CO stretching frequencies as a function of CO coverage to obtain singleton frequencies.

interactions, with the general finding that weaker metal– support interactions result in stronger metal–adsorbate interactions, influencing catalytic rates.⁶² This is in line with our CO adsorption work above, as red-shifts in CO bands are often indicative of stronger metal–CO interactions. Therefore, it is proposed that Pt particles in the Pt/SiO₂ series described here are electronically modified by the support, which results largely in ground state stabilization of D* (H*) surfaces on more basic supports, more so than transition state stabilization, and thus slower rates of C–H activation when D* is the MASI, as depicted in Figure 10.

Other work has been reported in favor of metal–support effects. For example, Haller and co-workers demonstrated that basic supports could influence the electron-richness of a Pt particle as assessed by both catalytic reactions (e.g., competitive toluene/benzene hydrogenation⁶³ and hydrogenolysis⁶⁴) and spectroscopy (e.g., X-ray spectroscopic measurement),⁶⁵ in accord with spectroscopies on other materials.^{41–43} Correlations between the acidic/basic nature of the support as assessed by CO adsorption and catalytic activity have been reported; these include heptane reforming,^{66–68} hydrogenolysis,^{69,70} aromatic hydrogenation,^{44–46} and catalyst deactivation studies.⁷¹ Catalytic studies on formic acid decomposition and water–gas shift have also demonstrated that sodium can influence activity and selectivity, in some cases accelerating rates due to the weakening of the formate C–H bond.⁷² Supported organometallic complexes have also been reported to be greatly modified by the support,

Figure 10. Depiction of proposed ground state stabilization (exaggerated for clarity) in Pt-500S catalyst due to stronger Pt-D* interaction compared to Pt-500 and Pt-0. The Pt surfaces with two open sites (middle species) have all been set to the same energy.

as shown by both catalytic measurements and CO adsorption.⁷³ Additionally, H/D exchange studies have been previously shown to be affected by changes in support.⁷⁴

It should be noted, however, that metal-support interactions have been a subject of debate.⁷⁵ One catalytic reaction studied in particular was *n*-hexane aromatization to benzene,^{76,77} a reaction which requires C–H bond activation. A Pt on K exchanged LTL-zeolite (Pt/K-L) was reported as a highly active and selective catalyst for conversion of *n*-hexane to benzene;⁸ this led to questions of why was this material better than others, and gave rise to many studies aimed to understand Pt/K-L's superior activity. Many explanations were proposed, including the pore geometry of the zeolite,⁷⁸⁻⁸⁰ Pt particle size,⁸¹ selectivity as a function of Pt coking and deactivation,⁸²⁻⁸⁵ and metal-support interactions as K-L is an electron-donating basic support. 63,75,86,87 Evidence for metal-support interactions in Pt/K-L were provided by FTIR spectroscopy with CO adsorption, which indicated that the Pt particles in Pt/K-L were electron-rich compared to other more acidic supports, like our work above. 50,51,53,58,88 Platinum on a nonzeolitic basic support, aluminum stabilized MgO, by Davis and Derouane, displayed similar conversions and selectivities compared with the aforementioned Pt/K-L catalyst,⁸⁹⁻⁹² and was originally proposed to behave similarly due to the basic nature of the MgO support; FTIR spectroscopy and CO adsorption

demonstrated red-shifts in the CO bands,⁹³ in accord with the basic nature of the support. Thus, there is a rich history of work on metal—support effects and the reported consequences they can have on catalytic activity, and our work provides additional data to demonstrate their potential effect on catalytic reactions. Our results do not rule out other effects, which may also play a significant role in influencing the activity of a catalytic metal.

CONCLUSIONS

In summary, we have demonstrated that the presence of Na on a silica-supported Pt catalyst can influence the rates of C-H activation in alkanes, as assessed by H/D exchange. Catalytic results in combination with CO adsorption FTIR spectroscopy suggest that metal-support interactions influence Pt reactivity, where more electron-donating basic supports produce more electron-rich Pt particles that undergo C-H activation more slowly. Kinetic and mechanistic studies indicate that C-H bond cleavage is preceded by D₂ desorption, resulting in an approximate inverse order dependence on D₂ and first order dependence on alkane, similar to previous findings.^{18,19} In accord with previous calorimetry data,⁶¹ we suggest that the principal reason for the difference in H/D exchange rates is a consequence of different Pt-D ground-state adsorption energies, where electron-donating supports cause Pt particles to have relatively stronger D* resting states (Figure 10). The TOFs and rate constants (k_{rxn}) of C-H activation have been quantified over a range of temperatures and conditions, which is useful as C-H activation is prevalent in hydrocarbon transformations, and required in catalytic alkane transformations. On the basis of the work cited above and our work here, a support can clearly impact the properties of supported metal particles, and H/D exchange is a sensitive technique to assess metal-support interactions. Seeing as adsorbate interactions of disparate species are often correlated with each other by well-known scaling relationships,⁹⁴ C-H activation experiments may be helpful to understand other hydrocarbon transformations, some of which were mentioned above,⁹⁵ and further research is required to show these correlations explicitly.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b03807.

Text and figures giving experimental details, characterization data, and reaction data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: aaron.sattler@exxonmobil.com. ORCID ©

Aaron Sattler: 0000-0001-5871-8646 Michele Paccagnini: 0000-0003-3511-9231 Michael P. Lanci: 0000-0001-8176-8895

Notes

The authors declare no competing financial interest.

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(24) Zaera has noted that different TOFs have been reported for different Pt catalysts, and proposed one reason is likely the different experimental conditions (e.g., D_2 pressure) and temperature. See ref 19. One additional reason, as seen in this work, is the effect of the nature of the Pt catalyst (e.g., Pt film, Pt/SiO₂, etc.).

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